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Dependence of Band Structure and Carrier Concentration of Metallic (13,13) and Semiconducting (13,0) Single Wall Carbon Nanotube on Temperature

(Kebergantungan Struktur Jalur dan Kepekatan Pembawa untuk Nanotiub Karbon Berdinding Tunggal yang Bersifat Logam (13,13) dan Semikonduktor (13,0) Terhadap Suhu)

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ABSTRACT

The electronic band structure, density of states (DOS) and carrier concentration of a (13,13) metallic and a (13,0) semiconducting Single Wall Carbon Nanotube (SWCNT) have been estimated and simulated by using the Fermi-Dirac distribution function. The energy dispersion E(k) relation for metallic SWCNT near the minimum energy is linear and the Fermi level was independent of temperature (T). On the other hand for semiconducting SWCNT the E(k) relation is parabolic. The normalized Fermi-Energy ($E_F - E_C$) in the nondegenerate regime is a weak (logarithmic) function of carrier concentration and varies linearly with T. In the degenerate condition, the Fermi level was independent of T and was a strong function of carrier concentration.

Keywords: Band structure; carbon nano-tube; carrier statistic; Fermi Level

ABSTRAK

Struktur jalur elektronik, ketumpatan keadaan dan kepekatan pembawa bagi nanotiub karbon berdinding tunggal (SWCNT) yang bersifat logam dan semikonduktor telah dianggarkan dengan menggunakan fungsi taburan Fermi-Dirac. Hubungan E(k) berdekatan dengan tenaga minimum adalah mendatar dan aras Fermi adalah bebas daripada pengaruh suhu (T) untuk SWCNTs yang bersifat logam. Manakala, untuk SWCNTs yang bersifat semikonduktor, hubungan E(k) adalah parabolik. Tenaga Fermi-ternormal ($E_F - E_C$) dalam regim tak-degenerat mempunyai fungsi ketumpatan pembawa (logaritma) yang lemah dan berubah secara linear dengan T. Dalam keadaan degenerat, aras Fermi tidak bergantung dengan T dan adalah satu fungsi yang bergantung kuat dengan kepekatan pembawa.

Kata kunci: Aras Fermi; nanotiub karbon; statistik pembawa; struktur jalur

INTRODUCTION

Due to the extraordinary electrical properties of single wall carbon nano tubes (SWCNTs), they have high potential in nano electronic applications (Wilder et al. 1998). To improve the utilization of SWCNTs in electronic applications, development of theoretical knowledge is one of the main challenges in this field. In fact, to foretell the functionality of these materials in electronic devices and circuits, we need to know more details about the electrical properties, such as band structure, electron density and electron transportation.

The diameter of a SWCNT is in the range of a fraction of nano-meter to a few nanometers (Vaseashta 2003). These sizes are comparable to the de Broglie wavelength of the electrons (Arora 2000). According to quantum hypothesis, when quantum effects become important, new phenomena would appear and the classical rules would not be valid any more. On the other hand, in quantum electronics and nanometer sizes, the density of electrons is almost in the degenerate regime and also the transportation of electrons can be considered ballistic (Akinwande et al. 2008; Lundstrom & Guo 2006).

Depending on the chiral vector, SWCNTs can be either semiconducting or metallic. Thus far, the fabrication of carbon nano tubes (CNTs) for most electrical applications, irrespective of synthesis methods, yields a mixture of both types (Chen et al. 2006). The electrical behaviour of such varieties in different temperature is not similar. Hence for characterization of devices, it is important to analyze the dependence of electrical properties on temperature in both types. In this work the carrier concentration and influence of temperature on the positioning of the Fermi level in semiconducting and metallic CNT in nondegenerate and degenerate regime are studied by applying quantum effects and using Fermi integral.

THEORETICAL ANALYSIS

CNT BAND STRUCTURE

The structure of a SWCNT can be imagined as a result of the rolling up of a graphite sheet (graphene), in which the diameter is about a fraction of nano-meter to a few nano-meters and length is up to several microns (Figure

1). Depending on the orientation of rolling up that is geometrically characterized by the chiral vector $\vec{C}$ where: $\vec{C} = \vec{n}a_1 + \vec{m}a_2$, they can be distinguished into three different types: Armchair, zigzag and chiral CNTs, with chiral vectors of (n,n), (n,0) and (n,m), respectively. From electrical standpoint, they can be divided into three groups: metallic, semi-metallic and semi-conductor. All Aarmchair CNTs are metallic. Again, if (n-m) is a multiple of three, the nanotube is semi-metallic, otherwise it is semiconducting type. By this segmentation, the (13,0) and the (13,13) carbon nanotubes are semiconducting and metallic types, respectively (Chen et al. 2003; Datta 2005).

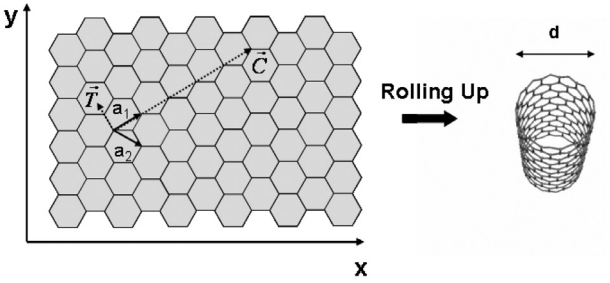


FIGURE 1. Illustration of how a graphene sheet is rolled up by chiral vector into a SWCNT. The length of CNT is much more than the de Broglie wavelength $L \rangle\rangle \lambda_D$ and diameter (d) is less than de Broglie wave length $d \langle\langle \lambda_D$

Under this definition, the band structure of a SWCNT can be understood in terms of the band structure of graphene. It is found that among the six corners of the Brillouin zone of each hexagon, there are only two independent Fermi points, it means all three atoms within a group are equivalent points and has one-third of a state. As a result, only two full states can be supposed in each hexagon. Moreover, by using a tight-binding theory, only one orbital ($2P_z$) is close enough to the Fermi level and has interaction with nearest neighbor (Datta 2005). The eigenvalues throughout the entire Brillouin zone of graphene are given by (Lundstrom & Guo 2006):

$$E\left(\vec{k}\right) = \pm|h_0| = \pm t \times \sqrt{1 + 4\cos\left(\frac{k_x\sqrt{3a}}{2}\right)\cos\left(\frac{k_y a}{2}\right) + 4\cos^2\left(\frac{k_y a}{2}\right)} \tag{1}$$

where $a = \sqrt{3}a_{c-c}$ and a_{c-c} = 1.42 Å is the nearest neighbor carbon-carbon *C-C* bond length of graphene, t = 2.7 (eV) is the nearest neighbor *C-C* tight binding overlaps energy and $k_{x,y}$ is wave vector component.

Once a graphene is rolled up into a CNT, the boundary conditions are imposed by the real physical structure of CNT. The requirements for satisfaction of boundary condition around the circumference of the nanotube can be expressed as:

$$\vec{k}.\vec{c} = 2\pi v.$$

The allowed values of k are quantized by boundary conditions and v is an integer value. Since there is no boundary condition along the axes of CNT, the permitted values of k are constrained along the circumferential direction and define a series of parallel lines, each corresponding to a different v. If one of these lines passes through one of the Fermi points, the CNT is called metallic nanotube, otherwise it is called semiconducting nanotube.

The number of hexagons in a unit cell of CNT (N) is given by: N=2n. Since each hexagon has two basis functions, the total number of states in a unit cell is equal to 2N. Each carbon atom donates one electron to the π-band, giving a total of 2N electrons which fill up half the states (exactly half full and half empty). It means the Fermi level is located at E=0. *S*ince we are interested in the dispersion relation $E(k)$ near the Fermi point, we expanded the above $E(k)$ relation throughout the Brillouin zone of graphene near the Fermi point by Taylor expansion of cosine function. The result is (Lundstrom & Guo 2006):

$$E(k) = \pm\frac{\sqrt{3ta}}{2}\sqrt{\left(k_x - k_{Fx}\right)^2 + \left(k_y - k_{Fy}\right)^2}. \tag{2}$$

By translating the origin of the reciprocal lattice to the Fermi point in (2), the $E(\vec{k})$ relation of the CNT can be estimated as:

$$E\left(\vec{k}\right) = \pm t\frac{3a_{c-c}}{2}\left|\vec{k}'\right| = \frac{t\,3a_{C-C}}{2}\sqrt{k'^{\,2}_{cv} + k'^{\,2}_{t}}, \tag{3}$$

in which the paramete k'_{cv} is the circumferential wave vector:

$$k'_{cv} = \frac{2}{3d}\left[3v - \left(n - m\right)\right]; \qquad v = 1, 2, \ldots, 2n,$$

and k'_t is the wave vector along the axis of the nanotube. k'_{cv} is quantized by the periodic boundary condition while for k'_t, any value, including zero, is permitted. The minimum band gap can be achieved as the difference in the energies between + and – branches of (3) at k'_t = 0 and when k'_{cv} is minimum. However, these minima for metallic and semiconducting nanotubes are different. In an armchair metallic CNT, the lowest subband with v=0 will always pass through the point $\left(0, 2\pi/3\right)$ regardless of the value of n. In a zigzag CNT, when n is a multiple of 3, the minimum of k'_{cv} is zero, results the zero band gap at k=0, such nanotube is called semi-metallic CNT. For a zigzag nanotube which n is not a multiple of 3, then a band gap occurs at k=0 and the nanotube is called semiconducting CNT. In recent case, the minimum of k'_{cv} is calculable as k'_{cv} =2/3d, where d is the diameter of the CNT (Lundstrom & Guo 2006):

$$d = \frac{\sqrt{3a_{c-c}}}{\pi}\sqrt{n^2 + m^2 + nm}. \tag{4}$$

By substituting these results into the (3) we get (5a) and (5b) for metallic and semiconducting types, respectively:

$$E(k) = \pm \frac{3a_{c-c}t}{2} k_t', \tag{5a}$$

$$E(k) = \pm \frac{3a_{c-c}t}{2} \sqrt{k_t' + \left(\frac{2}{3d}\right)^2}. \tag{5b}$$

The positive sign is for conductance band and negative sign is for the valance band. Rigorous attention to this formula illuminates several facts. Neither of $E(k)$ relations is parabolic but near the band minimum, all semi conducting nanotubes are alike and all metallic ones are similar (Karamdel et al. 2009) Equation 5a shows a one-dimensional linear dispersion, independent of (n,m) for metallic one but the similar equation for semiconducting CNT illustrates the dependent dispersion to n and m.

In armchair metallic and zigzag semi-metallic CNTs, the band crossing occur at $k_t = 2\pi/\ 3\sqrt{3_{c-c}}$ or at $k_t = 0$ respectively, but the minimum band gap of semiconducting type can be evaluated as:

$$E_G = \frac{2a_{c-c}t}{d}$$

By substituting this amount of E_G to (5b) the $E(k)$ relation for semiconducting CNT can be written as:

$$E(k) = \frac{E_G}{2} \sqrt{1 + \left(\frac{3kd}{2}\right)^2}. \tag{6}$$

Near the $k = 0$, for small arguments, the $E(k)$ relation can be expanded as:

$$E(k) = \frac{E_G}{2} + \frac{9a_{c-c}tk^2d}{8},$$

or:

$$E(k) = \frac{E_G}{2} + \frac{h^2k^2}{2m^*}, \tag{7}$$

where $m^* = 4h^2/9a_{c-c}td$ is supposed as the effective mass of CNT. It means that near k=0 the eigenvalues follow a parabolic function approximation.

DENSITY OF STATE AND CARRIER CONCENTRATION

In a CNT, two dimensions are less than de Broglie wave length and the length is much more than that (Figure 1). Consequently, CNT can be supposed as a quasi one dimensional device. We assumed thermal equilibrium condition and assumed just one sub band was accumulated. For such one-dimensional structures, the allowed states in k space are distributed with a density of $\left(\frac{L}{2\pi}\right)$ per unit K in x-coordinate (the direction of the CNT) for one spin. Hence for one dimensional device, the total density of allowed states in k-space including both spins could be defined as (Datta 2005):

$$N(k) = 2 \times \frac{kL}{2\pi}.$$

By using (7) and converting the k space to energy space, $N(E)$ which tells us the total number of states having energy less than E , can be calculated as:

$$N(E) = \frac{L}{\pi h}\left[2m_c(E - E_c)\right]^{1/2}. \tag{8}$$

The derivation of $N(E)$ gives the DOS per unit length along the axis of CNT:

$$\mathrm{DOS}(E) = \frac{dN(E)}{dE}.$$

As mentioned above, the metallic CNTs have band degeneracy at $k_t = 2\pi / 3\sqrt{3a_{c-c}}$ where the highest valence band and lowest conductance band cross the Fermi level, and there are $2n$ conduction bands and $2n$ valence bands. In these type of nanotubes, which are independent of their diameter and chirality, it follows that the density of states per unit length along the axis of CNT is a constant given by (Lundstrom & Guo 2006):

$$\mathrm{DOS}(E) = \frac{8}{3\pi a_{c-c}t}. \tag{9a}$$

Equation (9a) shows a uniform distribution of DOS in a metallic SWCNT. However, the result of derivation for semiconducting CNT can be written as

$$\mathrm{DOS}(E) = \frac{1}{\pi}\left(E - \frac{E_G}{2}\right)^{-\frac{1}{2}}\left(\frac{2m^*}{\hbar^2}\right)^{\frac{1}{2}}. \tag{9b}$$

The total carrier concentration in a band can be estimated from the DOS and Fermi function as (Neamen 2003):

$$n = \int_{E_C}^{\infty} \mathrm{DOS}(E).f(E)dE. \tag{10}$$

By substituting the DOS(E) and Fermi-Dirac distribution function expressions into the above formula, the carrier concentration can be evaluated for metallic (n_M) and semiconducting (n_s) nanotubes as (11a) and (11b), respectively:

$$n_M = \frac{8}{3\pi a_{c-c}t}\int_0^{\infty} \frac{1}{1 + e^{(E-E_F)/K_BT_L}}dE, \tag{11a}$$

$$n_s = \frac{1}{\pi}\left(\frac{2m^*}{\hbar^2}\right)^{1/2}\int_0^{\infty}\left(E - \frac{E_G}{2}\right)^{-1/2}\left(\frac{1}{1 + e^{(E-E_F)/K_BT_L}}\right)dE. \tag{11b}$$

These equations can be done analytically by using Fermi integral definition as:

$$n_M = \frac{8K_BT_L}{3\pi a_{c-c}t}F_0(\eta), \tag{12a}$$

$$n_S = \left(\frac{2m^*K_BT_L}{\pi\hbar^2}\right)^{1/2} F_{-1/2}(\eta). \tag{12b}$$

The Fermi integral of order *i* is defined as (Neamen 2003):

$$F_i(\eta_D) = \frac{1}{\Gamma(i+1)} \int_0^\infty \frac{x^i}{e^{(x-\eta)}+1} dx, \quad (13)$$

where $\eta = (E_F - E_C)/K_B T$ (K_B is the Boltzmann constant and T is the temperature) and $\Gamma(x)$ is called gamma function which is defined as:

$$\Gamma(x) = \int_0^\infty t^{(x-1)} e^{-1} dt.$$

It is shown that if the Fermi level lies in the band gap more than $3k_BT$ from either band edges, the CNT is said to be nondegenerate, otherwise it is degenerate. In nondegenerate condition the Boltzmann approximation of distribution function becomes less valid and the equations for the Fermi level position are no longer quite as accurate (Neamen 2003).

Results and Discussion

For studying and analyzing the carrier concentration in both types of CNTs and the effect of temperature on these parameters, a set of simulation have been done by using MATLAB and ATOMISTIX software's. The programming and simulation are based on above formulas and mathematical methods for solving them.

In the case of nondegenerate condition the Fermi integral can be simplified as (Arora 2006):

$$F_i(\eta) = e^{\eta}. \quad (14)$$

While for the degenerate regime (13) could be simplified as below:

$$F_i(\eta) = \frac{1}{\Gamma(i+1)} \times \frac{\eta^{(i+1)}}{(i+1)}. \quad (15)$$

The nondegenerate and degenerate approximations (14 and 15) have been compared with the original Fermi integral. As shown in Figure 2 the Fermi order -1/2 ($\Gamma_{-1/2}$) can be approximated by exponential of η when $\eta \leq -3$ in nondegenerate regime, and for $\eta \geq 3$ can be approximated by $2/\sqrt{\pi} e^{1/2}$ in degenerate regime. These results confirm the approximated formula in (14) and (15).

Figure 3 shows the simulation results for dispersion relations of a (13,0) semiconducting and a (13,13) metallic CNTs. As we see, the semiconducting CNT has a band gap but the dispersion relation for the subbands of metallic type has no gap in the energy spectrum. These are in good agreement with expected results of theoretical analysis of (5).

Due to the crossing point (zero bandgap) of the lowest conductance and highest valence subbands of metallic SWCNT, in ambient temperature all $2P_z$ orbitals (valance electrons) could obtain enough energy to excite to the conduction band. In such condition the number of carriers can be estimated as 2N per unit cell. Figure 4 shows the simulation results for carrier concentration of a (13,13) metallic CNT at $T = 300$ K. This result shows an electron density of 2.16 Å^{-3} which were uniformly distributed allover of the CNT.

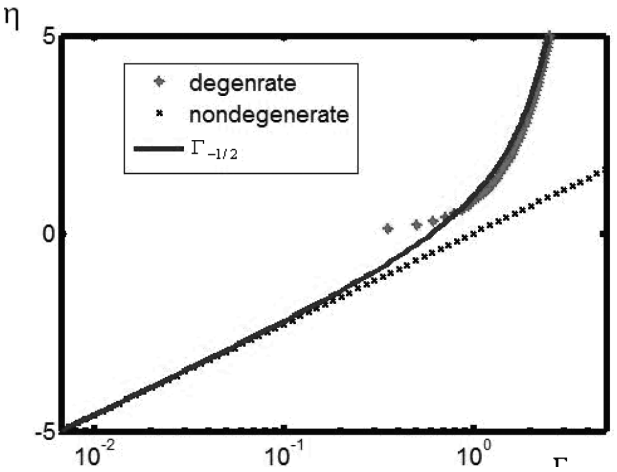
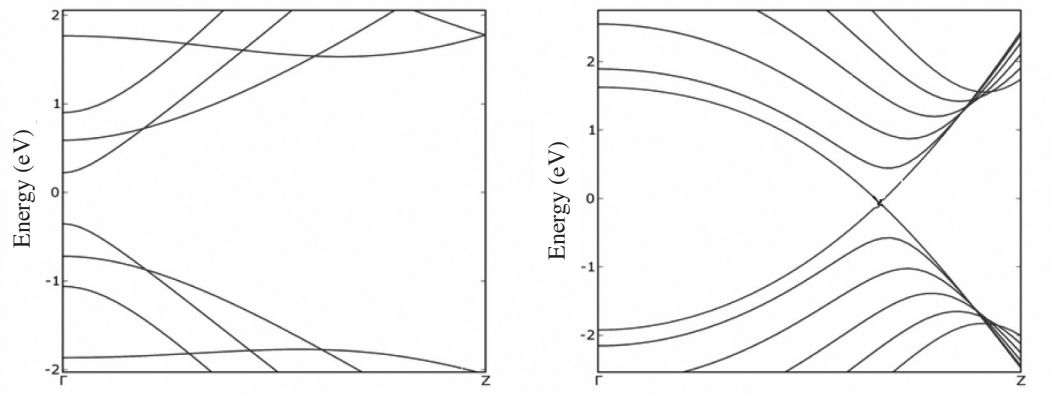


FIGURE 2. The simulation results Compares the Fermi-Dirac integral ($\eta_{-1/2}$), e^{η} and $\eta^{1/2}$



(a) (b)

FIGURE 3. Band structure of (a) a (13,0) semiconducting SWCNT and (b) a (13,13) metallic SWCNT

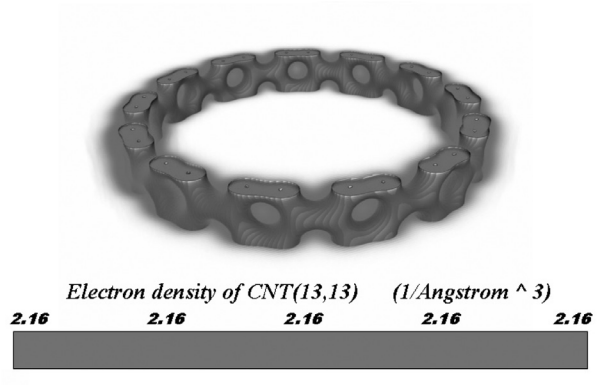


FIGURE 4. Simulation result for carrier concentration of a (13,13) metallic CNT shows a uniformly distribution of electrons all over of CNT (2.16 Å^{-3})

However, for semiconducting type, the Fermi integral of (12b) must be solved for nondegenerate and degenerate regimes. By using (14) for nondegenerate condition, the carrier concentration of semiconducting type can be simplified as:

$$\eta_1 = N_{c1} e^{-\left(\frac{E_C - E_F}{K_B T}\right)}, \tag{16}$$

where is the total energy of electrons near the minimum energy band:

$$E_C = E_{C0} + \varepsilon_{0y} + \varepsilon_{0z} + \frac{\hbar^2 k_x^2}{2m^*},$$

and

$$N_{C1} = \left(\frac{2m^* K_B T_L}{\pi \hbar^2}\right)^{1/2},$$

is the one dimensional DOS.

In the degenerate condition, by substituting the (15) into the (12b) the carrier concentration can be written as:

$$\eta_1 = \left(\frac{8m^*}{\pi^2 \hbar^2}\right)^{1/2} \cdot \left(E_f - E_C\right)^{1/2}. \tag{17}$$

According to these results, is a weak (logarithmic) function of carrier concentration in the nondegenerate regime but is a strong function of carrier concentration in strongly degenerate statistics (Arora 2006). The simulation results for carrier concentration of a semiconducting (13,0) CNT at $T = 300\ K$, by using of (12b), is shown in Figure 5. Further consideration in the color bar of this figure reveals that much less free electrons are distributed in the semiconducting type in compare with the metallic type.

CONCLUSIONS

The electronic band structures, density of state and carrier concentration of metallic SWCNT and a semiconducting

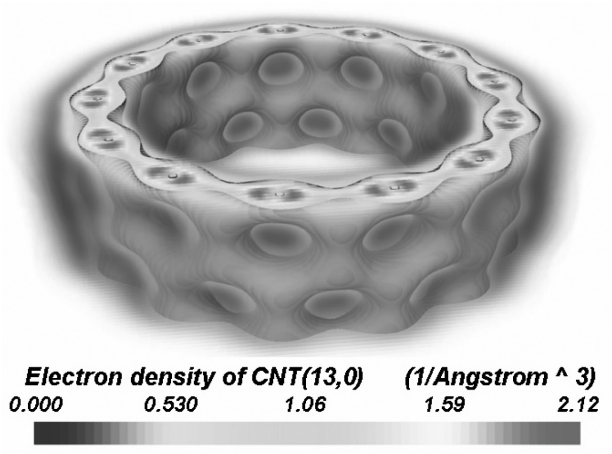


FIGURE 5. Simulation result for carrier concentration of a (13,0) semiconducting CNT shows a few free electron in the structure of CNT

SWCNT have been studied by using the Fermi-Dirac distribution function. In a metallic SWCNT the subbands do not have any gap in the energy bands and electrons spread uniformly all over of the CNT for every T, which means the Fermi level was independent of T. In metallic type the electron concentration has been estimated as 2.16 Å^{-3}. In a semiconducting CNT there is a band gap in the energy bands and electron concentration for degenerate and nondegenerate conditions have been calculated by approximation of Fermi integral. The normalized Fermi energy ($E_F - E_c$) as a function of normalized carrier concentration (n / N_C) for nondegenerate and degenerate regimes showed that in the nondegenerate regime, ($E_F - E_c$) was a weak (logarithmic) function of carrier concentration, but varies linearly with temperature. In the degenerate condition, the Fermi level was independent of temperature and was a strong function of carrier concentration.

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